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A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY,
IN THE UNIVERSITY OF MICHIGAN

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CHARACTERISTIC L ABSORPTION OF X-RAYS FOR ELEMENTS OF ATOMIC NUMBERS 62 TO 77.

By J. M. CORK.

ABSTRACT.

Characteristic L x-ray absorption wave-lengths for nine elements of atomic numbers 62 to 77.—Since the L absorption wave-lengths had been determined for elements of atomic numbers 55 to 60, 74, and 78 to 92, it was of interest to fill in the gaps. Accordingly compounds of *samarium* (62), *gadolinium* (64), *dysprosium* (66), *erbium* (68), *ytterbium* (70), *tantalum* (73), *tungsten* (74), *osmium* (76) and *iridium* (77) were precipitated upon filter paper and placed in the path of x-rays from the tungsten target of a Coolidge tube. In each case the three L absorption bands together with the emission lines of W were photographed, using a calcite crystal which was rotated with a constant angular velocity. The wave-lengths and the frequency numbers divided by the Rydberg constant, ν/N , are tabulated. The energy levels within the atoms corresponding to the different absorption limits computed in terms of ν/N from the absorption and emission frequencies, are also given. The regular doublet differences $\Delta(\nu/N) = (\nu_{L_2} - \nu_{L_1})/N = L_2 - L_1$ are found to agree well with the values calculated from the Sommerfeld formula.

The variation of the regular doublet frequency differences $L_2 - L_1$, $M_2 - M_1$, $M_4 - M_3$ with atomic number is given very closely by the series expressions developed by Sommerfeld. For elements of high atomic number, Z , these series do not converge very rapidly. For the range of elements mentioned in this paper the empirical expression $\Delta(\nu/N) = KZ^5$ is found to hold within the experimental limits where K has the following values: 4.44×10^{-8} for $L_2 - L_1$, 1.97×10^{-9} for $M_2 - M_1$, and 9.60×10^{-9} for $M_4 - M_3$.

Suggested notation for x-ray emission lines.—Instead of the present conflicting notations, it is suggested that the symbol for each emission line designate the initial and final energy levels; for example the line produced by an electron shifting to the L_1 from the M_5 orbit might be denoted by $L_1\beta_5$ instead of $L\ell$ or L_e .

THE three L absorption wave-lengths for elements of atomic numbers 55 to 60 have been determined by Hertz;¹ and for elements of atomic numbers 74 and 78 to 92 by deBroglie² and Duane.³ As these data are of great significance in building theories of the inner atomic structure, alternate elements in the gap, atomic numbers 62 to 77 have been investigated.

Most of the elements investigated are rare earths, compounds of which were isolated by Professor James of New Hampshire State College. The compound of the element used, shown in Table I., was uniformly

¹ Hertz, Z. fur Phys., 3, 1, p. 19.

² deBroglie, J. de Phys., 6, p. 161.

³ Duane, Proc. Nat. Acad. Sci., 6, p. 509.

distributed upon a filter paper and placed in the path of the x-ray beam at the first slit between the x-ray tube and the calcite crystal. The crystal was rotated by means of a clock mechanism over a small arc, and the reflected x-ray beam was examined photographically.

TABLE I.
Compounds Used.

At. No.	Element.	Compound.
62.....	Samarium	Oxalate
64.....	Gadolinium	Oxalate
66.....	Dysprosium	Oxalate
68.....	Erbium	Oxalate
70.....	Ytterbium	Oxalate
73.....	Tantalum	Tantallic acid
74.....	Tungsten	Tungstic acid
76.....	Osmium	Osmic acid
77.....	Iridium	Chloride

A Coolidge tube provided with a tungsten target was used as a source of x-rays and there thus appeared upon the photographic plate the emission lines of tungsten as well as the absorption lines of the element under investigation. A 500-cycle generator with step-up transformer was used as the power supply. The secondary of the transformer was connected to the x-ray tube through a kenotron rectifier, while a high voltage condenser was connected in parallel with the x-ray tube. The capacity of the condenser was sufficiently high to result in an almost constant direct voltage being applied to the tube. In most of the work a tube current of 7 milliamperes at 30,000 volts was used. This was found to be about the maximum allowable power input for continuous operation of the tubes. An air blast was directed against the tube to aid in cooling. At this power input a time of exposure of from 30 to 40 hours was necessary to secure satisfactory plates. This long time was required because x-rays of the wave-lengths worked with were largely absorbed in the glass walls of the x-ray tube; the time of exposure necessary would have been greatly reduced by using a tube provided with a thin window.

The wave-lengths of the tungsten emission lines have been determined by Overn,¹ Duane,² Siegbahn,³ and others, with very good agreement for the more prominent lines. These were used as reference lines in measuring the wave-lengths of the absorption edges. The values of the wave-lengths used, expressed in Ångstrom units, are shown in Table II.

¹ Overn, *PHYS. REV.*, 9, 137, 1919.

² Duane, *PHYS. REV.*, 15, 532.

³ Siegbahn, *Ph. Z.*, 20, p. 533.

TABLE II.
X-ray Spectrum of Tungsten.

Wave-lengths Observed by			Wave-lengths Used.	Notation of		Notation Suggested.
Overn.	Siegbahn.	Duane.		Siegbahn.	Sommerfeld.	
0.9168			0.9168			
1.0263	1.02647	1.0261	1.0263	γ_4	ψ	$L_3\delta_3$
1.0596	1.05965	1.0596	1.0596	γ_3	x	$L_3\gamma_6$
1.0659	1.06584	1.0655	1.0657	γ_2	x'	$L_3\gamma_6$
1.0967	1.09533	1.0965	1.0960	γ_1	δ	$L_2\gamma_4$
1.1302	1.1284		1.1290	γ_5	κ	$L_2\gamma_7$
1.2434	1.24191	1.24193	1.2420	β_2	γ	$L_1\gamma_3$
1.2598	1.2600	1.2601	1.2600	β_3	φ	$L_3\beta_3$
1.2793	1.27917	1.2789	1.2792	β_1	β	$L_2\beta_2$
1.2872	1.2871		1.2872	β_6	i	$L_1\gamma_7$
1.2984	1.29874	1.2985	1.2986	β_4	φ'	$L_3\beta_4$
1.4731	1.47348	1.4731	1.4732	α_1	α	$L_1\beta_1$
1.4839	1.4845	1.4839	1.4840	α_2	α'	$L_1\beta_2$
	1.67505	1.6756	1.6753	l	ϵ	$L_1\beta_5$

A distance of 0.1 cm on the plates corresponded to a difference in wave-length of about .01 Ångstrom unit. The probable error in the measurement of the lines was about .002 cm, corresponding to an accuracy of about .0002 Å. However the wave-lengths of some of the tungsten emission lines are not agreed upon to that degree of accuracy. In a few cases the absorption limit falls very close to an emission line. For the longer wave-lengths where extrapolation is necessary, the error in L_1 and L_2 may be as large as .002 Å, and for L_3 , which is not so clear, the error may be larger.

TABLE III.

Atomic Num- ber.	$A_1.$			$A_2.$			$A_3.$		
	$\lambda.$	$\nu/N.$	$(\nu/N)^{1/2}.$	$\lambda.$	$\nu/N.$	$(\nu/N)^{1/2}.$	$\lambda.$	$\nu/N.$	$(\nu/N)^{1/2}.$
62.....				1.701	535.7	23.14	1.608	566.7	23.80
64.....	1.699	536.4	23.16	1.550	587.9	24.25	1.470	619.9	24.89
66.....	1.576	578.2	24.05	1.435	635.0	25.20	1.362	669.1	25.87
68.....	1.478	616.5	24.83	1.336	682.1	26.12	1.265	720.4	26.84
70.....	1.386	657.5	25.64	1.242	733.7	27.09	1.171	778.2	27.90
73.....	1.253	727.3	26.98	1.111 ₈	819.6	28.63	1.058	861.3	29.35
74.....	1.211 ₂	752.3	27.43	1.071 ₈	850.2	29.17	1.023	890.8	29.85
76.....	1.138	800.7	28.30	.998 ₅	912.6	30.21	.951 ₆	957.7	30.94
77.....	1.103 ₆	825.7	28.74	.965	944.3	30.73	.919 ₆	991.0	31.47

Table III. shows the mean values of wave-lengths observed, expressed in Ångstrom units. In addition, the values of ν/N and of the square root of ν/N are given, where ν is the number of waves per cm and N is

the Rydberg constant

$$\frac{2\pi^2 e^4 m}{h^3 c} = 109,740,$$

e and m being respectively the charge and mass of an electron, h the Planck constant 6.55×10^{-27} erg sec, and c the velocity of light.

TABLE IV.

At. No.	$L_2 - L_1$.	Calc. $\Delta(\nu/N)$.	$L_\beta - L_{\alpha'}$.
62.....		43.85	43.95
64.....	51.5	50.65	50.64
66.....	56.8	58.25	58.27
68.....	65.6	66.66	66.80
70.....	76.2	76.29	76.24
73.....	92.3	92.34	92.66
74.....	97.9	98.46	98.54
76.....	111.9	111.33	111.08
77.....	118.6	118.30	118.64

Table IV. shows the $L_2 - L_1$ (regular doublet) frequency difference expressed as $\Delta\nu/N$ compared with values computed from the Sommerfeld formula,¹ and the frequency difference of the L_β and the $L_{\alpha'}$ emission lines. The agreement of the three columns is within experimental limits.

The Sommerfeld formula was developed on the assumption that the stationary states of the electrons within the atom are characterized by two quantum numbers. One is called the azimuthal quantum number n which has positive integral values, zero excluded; the other is called the radial quantum number n' and may be zero or a positive integral number. For electrons in the L shell the sum of n and n' is taken as 2. This leads to two possible modes of rotation for the electrons, in one of which, $n = 2$, $n' = 0$, the electronic path is circular, while in the other, $n = 1$, $n' = 1$, the path is an ellipse.

The second postulate states that the frequency of the radiation emitted or absorbed by atoms is determined by the total energy difference between the initial and final states of the atom doing the emitting or absorbing:

$$(1) \quad W_f - W_i = h\nu.$$

Sommerfeld showed that although the quantum sum for electrons characterized by $n = 2$, $n' = 0$ and $n = 1$, $n' = 1$ is the same, if the variation of mass with velocity as required by relativity theory be considered the energy of the two states is not the same, being less in the latter case. The general expression for the total energy of an electron of an orbit characterized by azimuthal quanta n and radial quanta n'

¹ Sommerfeld, *Atombau*, 3d Ed., p. 607.

is given as:

$$(2) \quad W_{n, n'} = hN(E/e)^2 \left[\frac{1}{(n + n')^2} + \frac{\alpha^2}{(n + n')^4} \left(\frac{E}{e} \right)^2 \left(\frac{1}{4} + \frac{n'}{n} \right) + \dots \right],$$

where $\alpha^2 = 4\pi^2 e^4 / h^2 c^2 = 5.32 \times 10^{-5}$ and (E/e) is the ratio of the charge on the nucleus to that of an electron. If values of $n = 2$, $n' = 0$ and $n = 1$, $n' = 1$ be substituted in Eq. (2) and the difference of the two equations be divided by Nh , the following equation is obtained:

$$(3) \quad \Delta \frac{W}{Nh} = \Delta \frac{\nu}{N} = \left(\frac{E}{e} \right)^4 \frac{\alpha^2}{2^4} \left[1 + \frac{5}{2} \frac{\alpha^2}{2^2} \left(\frac{E}{e} \right)^2 + \frac{53}{8} \cdot \frac{\alpha^4}{2^4} \left(\frac{E}{e} \right)^4 + \dots \right].$$

This equation should then give the difference in ν/N to be expected in the transfer of electrons from the same initial orbit to these two end orbits or conversely from these two orbits to the same final energy level. By writing in the right-hand member of Eq. (3) $(Z - s)$ for E/e , where Z is the atomic number of an element and s an arbitrary parameter, and equating this to $\Delta\nu/N$ obtained by taking the difference of the numbers ν/N for the L_β and $L_{\alpha'}$ emission lines of that element, Sommerfeld obtained an average value for s of 3.5. This value was constant for elements from atomic number 41 to atomic number 92, and was interpreted as a neutralizing effect upon the nucleus due to other electrons of the atom.

When an electron is removed from its orbit to the periphery of the atom the total energy of the system is increased by a definite amount and hence a definite frequency will be absorbed. Thus the L_1 absorption frequency means the removal of an electron from the circular orbit ($n = 2$, $n' = 0$), while the L_2 absorption frequency represents the removal of an electron from the elliptical orbit ($n = 1$, $n' = 1$). It should not be expected however that Eq. (2) divided by hN would give the observed values of ν/N for the absorption limits L_2 and L_1 . For elements of large atomic number the problem is much more difficult. The work in taking an electron to the surface is influenced by the presence of the many other electrons; and the energy of every electron is probably altered by the removal of one of their number. It is the total change in energy that must be considered and to calculate this would require a knowledge of the distribution of all the electrons in the atom. The fact that the difference expression Eq. (3) can be made to fit observed values so well over a wide range of elements indicates that any effect due to other electrons is about the same whether an electron leaves the L_1 or L_2 levels and hence disappears on taking the difference.

The meaning of the L_3 absorption limit is problematical.¹ Its fre-

¹ Wentzel, Z. fur Phys., 6, 2, p. 84 et seq.

Smekal, Z. fur Phys., 5, 2, p. 121 et seq.

Bohr, Z. fur Phys., 9, 1, p. 1.

quency being greater than that of L_1 and L_2 indicates that the energy change accompanying it is greater than in the two previous cases. Smekal and Wentzel have suggested that the stationary states should be determined by three quantum numbers instead of two, thus making possible a larger number of energy levels for a given quantum sum. Bohr has suggested that the L electrons may be divided into two subgroups; electrons in leaving one of the subgroups give rise to the single L_1 absorption frequency, while in leaving the other, which represents a more stable or tightly bound group, it is possible for the electrons left to arrange themselves in two distinct configurations representing different energy totals in the final state. This may perhaps be brought about by electrons travelling in the eccentric orbits of the outer electron shells coming within the L shell.

Figure 1 shows the values of the square root of ν/N , together with

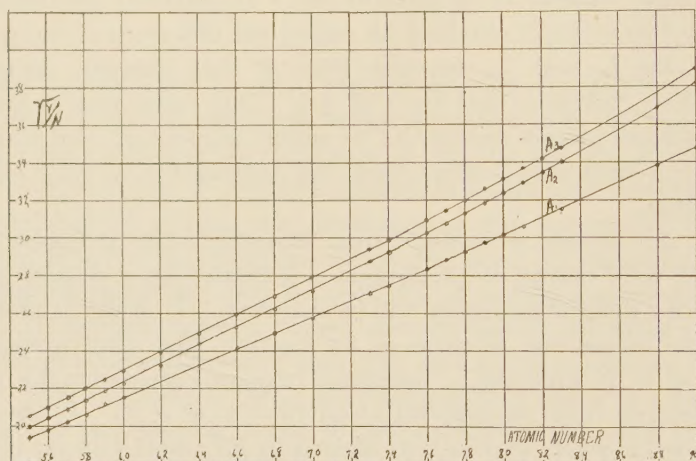


FIG. 1. $\sqrt{\nu/N}$ for L_1 , L_2 , and L_3 as a function of atomic number.

the values of other observers, plotted as a function of atomic number. By taking into account the nuclear defect due to other electrons and the relativity correction, the deviation of these curves from the straight line Moseley relation may be qualitatively explained. If in Eq. (2) the effect of other electrons be neglected as well as the relativity correction, the first term gives the Moseley relation:

$$(4) \quad \sqrt{\frac{W}{hN}} = \sqrt{\frac{\nu}{N}} = 1/2 \left(\frac{E}{e} \right).$$

If values of $(\nu/N)^{1/2}$ were plotted against E/e , a straight line of slope $1/2$ would be obtained. It is apparent that all three observed curves lie

below this straight line as would be expected if $(Z - s)$ had been used instead of E/e . By using additional terms of Eq. (2) the curves would deviate from straight lines with an upward curvature for increasing atomic numbers.

The fact that $\Delta(\nu/N)^{1/2}$ for $L_3 - L_2$ is practically constant would by Bohr's theory indicate that the difference in the neutralizing effect upon the nucleus for the two configurations after the removal of an electron from the L_2 subgroup is a constant for a wide range of elements.

By combining the absorption frequencies with the emission frequencies of each element,¹ the energy levels of the various electronic orbits may be determined. Table V. shows these energy levels expressed in terms of

TABLE V. *Values of ν/N .*

Z.	K.	L_1 .	L_2 .	L_3 .	M_1 .	M_2 .	M_3 .	M_4 .	M_5 .
62	3457		535.7	566.7		78.5	101.3		
64	3710	536.4	587.9	619.9	90.0	92.8	116.1	126.9	
66	3972	578.2	635.0	669.1	99.7	101.7	126.5	138.6	
68		616.5	682.1	720.4	104.6	107.2	135.0	149.4	152.9
70		657.5	733.7	778.2	111.0	114.6	149.1	165.7	172.5
73		727.3	819.6	861.3	126.9	131.1	161.9	181.7	183.7
74	5118	752.3	850.2	890.8	133.9	138.1	167.6	189.1	207.8
76	5414	800.7	912.6	957.7	144.2	149.2	183.6	209.4	
77		825.7	944.3	991.0	149.9	155.3	190.2	216.4	

Z.	N_1 .	N_2 .	N_3 .	N_4 .	N_5 .	N_6 .	N_7 .
62				6.8	16.6		
64			13.1	14.1	31.6		
66	3.8	3.9	15.5	13.8	25.1		
68	.7	.9	13.4	13.7	26.5		
70	(-1.2)	(-.8)	12.1	13.3	32.0		
73	1.0	1.1	15.6	15.9	30.0		
74	3.2	3.0	18.5	18.4	30.9	35.8	43.4
76	3.6	3.4	20.1	21.3			44.4
77	4.0	4.2	21.3	22.4	38.4		47.9

ν/N for the elements investigated. As some of these computations require the combination of three measurements the errors are correspondingly large. For example $N_1 = L_1 - L_\alpha - M_\alpha$.

From Eq. (3) the variation of the regular doublet difference $L_2 - L_1 = (\nu_{L_2} - \nu_{L_1})/N$ with effective atomic number may be obtained. Similar expressions are developed by Sommerfeld for the regular doublet differences $M_2 - M_1$, $M_4 - M_3$, etc. By effective atomic number is meant the atomic number minus a nuclear defect. This nuclear defect is a constant for any particular doublet over a range of elements from atomic number 41 to atomic number 92; thus 3.5 for $L_2 - L_1$, 13.0 for $M_2 - M_1$,

¹ Hjalmar, Z. fur Phys., 3, 4, p. 262; 7, p. 341.

8.3 for $M_4 - M_3$, etc. As an approximate expression Sommerfeld mentions the first term of the series which on evaluating the constants for $L_2 - L_1$ is $\Delta(\nu/N) = 3.32 \times 10^{-6}(Z - 3.5)^4$. For elements of large atomic numbers the series does not converge rapidly and the first term alone gives values of $L_2 - L_1$ that are about one fourth too small. It may be of interest that the empirical expression $\Delta(\nu/N) = KZ^5$ approximates quite closely the observed values over the range of elements mentioned in this paper for $L_2 - L_1$ and over a wider range for $M_2 - M_1$ and $M_4 - M_3$. K has the following values: 4.44×10^{-8} for $L_2 - L_1$, 1.97×10^{-9} for $M_2 - M_1$ and 9.60×10^{-9} for $M_4 - M_3$.

It is suggested that as soon as an emission line can be definitely related to the transfer of an electron from one orbit to another, this knowledge might well serve as a basis for a notation to replace the present conflicting systems. Such a notation is suggested in Table II. for the tungsten emission lines. The capital letter with subscript gives the end orbit while the Greek letter tells from what group of outer orbits the electron came. The subscript gives the particular orbit of the group. The L group is distinguished by the letter α , the M group by β , the N group by γ , etc. Thus the line designated by Siegbahn as Ll and by Sommerfeld as L_ϵ is produced by an electron arriving at the L_1 orbit from the M_5 orbit. It is accordingly denoted as $L_1\beta_5$. While this notation is more cumbersome, it possesses the advantage of giving complete details without further effort.

UNIVERSITY OF MICHIGAN,

October 7, 1922.

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